Optical emission characteristics of carbon plasma produced by single- and double-pulse laser ablation

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The effect of additional laser irradiation on the optical emission of laser ablated carbon plasma have been examined to define plasma conditions for the controlled synthesis of carbon structures.

1. Introduction

Laser ablation carbon plasmas have been intensively examined during the last years to define plasma conditions for the synthesis of carbon structures with unique properties in particular, fullerenes and nanotubes [1,2]. The physical properties of plasma plume, such as species concentrations and temperature, directly affect the properties of the material being formed. Successful synthesis is strongly dependent on the formation of atomic and molecular species with required chemistry and energy. For selection of optimal plasma conditions the detailed understanding the basic physical and chemical processes governing the ablation plume composition and reliable methods for controlling of the relative amounts of plume species are needed. Different laser-induced effects through mechanisms of laser-surface and laser-plasma interactions may be useful for the control of ablation plume characteristics. In this context, the double-pulse laser ablation technique leading to better coupling of laser pulse energy to the target and ablated matter is of great interest. This paper presents time-resolved emission spectroscopic studies of C_2 and C_3 species produced by single- and double-pulse laser ablation of graphite in helium atmosphere. It is suggested [1] that the small carbon molecules may serve as feedstock for carbon nanotubes formation. In this connection the study of the dynamics of these species in the plume is important for establishment of the growth mechanisms of carbon nanotubes in the laser ablation processes.

2. Experimental

The experiments were carried out using a set-up described elsewhere [3]. The Nd-YAG (1064 nm, 10 ns, $5 \cdot 10^8$ W/cm^2) laser radiation in combination with the second harmonic (532 nm, $5 \cdot 10^7$ W/cm^2) radiation of another Nd-YAG laser at different temporal delays between pulses were employed for ablation. The laser beams were focused on the surface of the graphite sample placed in the chamber under helium environments. The pressure of the helium atmosphere was about 600 Torr. In the experiment the sample was a new surface for each pulse that was achieved by rotating the target.

Spectroscopic characterization of the ablated plume was performed by the time resolved emission spectroscopy and laser-induced fluorescence methods. The details of these diagnostic techniques were described in [4].

Optical observation of the plasma emission was performed by imaging the section of the plasma plume onto the entrance slit of monochromator equipped by the fast photomultiplier. The detection of the photomultiplier signals was accomplished by a digitizer, connected to a personal computer for data processing, storage and analysis. The review emission spectra of plasma were recorded in the UV and visible region using a spectrograph with a reciprocal dispersion of 1.6 nm/mm. Kinetic energies of ablated species were determined by measuring their time-of-flight characteristics.

3. Results and discussion

The plasma emission spectra (300-700nm) were recorded and compared for different ablation regimes (single pulse and double pulse in coincidence and in sequence at various delays between pulses and laser fluences). The major species including CI, CII, and C_2, C_3 radicals within the plume have been identified. The spectra were dominated by the C_2 Swan bands ($d^3\Pi_g$ - $a^3\Pi_u$). The recorded Swan bands included $\Delta\upsilon$ = +1 (470-475 nm); $\Delta\upsilon$ = 0 (510-516nm); $\Delta\upsilon$ = -1 (550-565 nm); and $\Delta\upsilon$ = -2 (595-615 nm); where $\Delta\upsilon$ is the difference of the vibrational quantum numbers between the upper and the lower states of transition. The emission in the wavelength range 390 - 410 nm was identified as the C_3 (Comet Head System: $A^1\Pi_u$ - $X^1\Sigma_u^+$). The C_2 high-pressure bands in the spectra were also recorded including the (6 - 7) band at 543.4 nm and (6 - 8) band at 589.9 nm. The high-pressure bands are known to be part of the Swan system with $\upsilon' = 6$ levels excited at relatively high pressures.

Transient emissions from the plume zone (1 mm from the target) were detected at 543.4 nm, at 473.7 nm, (C_2 Swan system), and at 404.9 nm (C_3 Comet Head System). The emission of C_2, C_3 molecules persisted for 3-5 μs after the laser pulse, although the radiative lifetime of the upper states much shorter (only about 100 ns for C_2 Swan bands). This implies that formation of the excited carbon species must continue for at least a few microseconds after the laser pulse. A maximum of emission is reached not later than after 300 ns. Except for amplitudes there were no significant differences between wave forms of molecular emissions originated from different electronic-vibrational levels as well as between the temporal shapes of C_2 and C_3 bands.

The coupling of the second laser beam into the laser-ablated plume caused changes of molecular plume dynamics. The temporal evolution of the emission of C_3 molecules is presented in Fig.1. As can be seen from Fig.1 the C_3 band intensity in plasma produced by the sequence of two laser pulses is larger in comparison to the single pulse mode. In contrast to the ionic lines in double-pulse laser produced plasma [5] the enhancement of molecular emission was observed in a rather small interval of pulse separations (0-5 μs for C_3 molecules). It should be noted that when two pulses were fired simultaneously the effect was more than just additive both for the C_3 and C_2 band intensities.

The effect of preplasma produced by the first (IR) laser pulse on the spectrum of plume formed by the second (green) laser depends on the time delay between pulses. Fig.2 presents the ratio of the emission amplitudes of C_2, C_3 molecules from the 1064-532 nm double-pulse and from the 532 nm single-pulse laser ablation plasma versus the temporal delay between two laser pulses (Δt). It should be noted that for $\Delta t \leq 2$ μs the intensity of C_2 emission from the double-pulse plasma increases but for $2 \leq \Delta t < 30$ μs decreases. The intensity of C_3 emission from the double pulse produced plasma increases until the time separation between laser pulses does not exceed of 5 μs. For time delays $\Delta t > 5$ μs the presence of preplasma does not exert influence on the emission characteristics of C_3 molecules. As for C_2 emission it ceases to be influenced by the preplasma for time delays $\Delta t > 30$ μs. So, plasma produced by the first laser pulse seems to decay completely after 30 μs.

Several mechanisms may be responsible for the observed features of double-pulse laser-produced plasma spectra. The enhancement of the molecular emission may be related to the production of the excited C_2, C_3 molecules through the decomposition of carbon clusters (fullerenes) and evaporation of the particulates (soot particles) formed after action of the first laser pulse. The Rayleigh scattering measurements supported the presence of particulates in the plume. The subsequent laser pulse may fragment carbon clusters as well as heat and evaporate carbon particles. It is known that electronically excited C_2 is a photo-fragmentation product of laser-excited fullerenes [6]. Laser vaporization of suspended particles also generates C_2 and other small carbon molecules. It should be noted that surface temperature increasing after the first laser pulse resulting in enhancement of the amount of vaporized species may also contribute in observed emission features.

So, experiments demonstrate increased plasma emission, higher degree of particle atomization in dual-pulse ablation regime at the optimal pulse separations compared to the plasma produced by one laser. The double-pulse laser ablation enables the plasma to be further affected in a controlled way. By proper selection of the pulse separations and wavelengths in the sequence of two laser pulses the parameters of the near-surface plasma can be adjusted to optimize its applications.

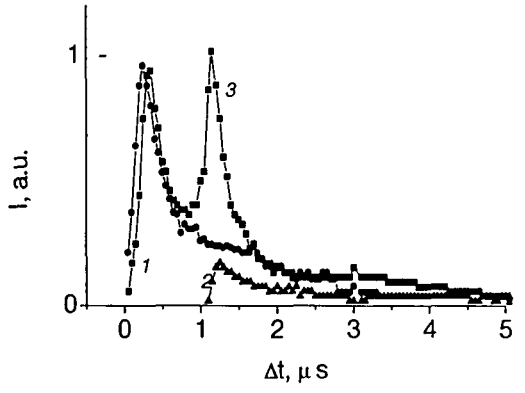

Fig.1. Time-resolved C_3 band emission intensities (λ=404.9nm) for the cases of single-pulse 1064 nm laser ablation (*1*), single-pulse 532 nm laser ablation (*2*), and double-pulse mixed wavelength

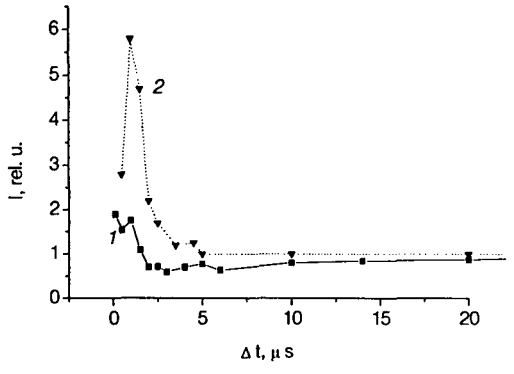

Fig.2. The ratio of the emission amplitudes of C_2 (*1*) and C_3 (*2*) molecules from the 1064 - 532 nm double pulse and from the 532 nm single-pulse laser ablation plasmas as a function of the temporal delay between laser pulses (Δt).

References

[1] C.D.Scott, S.Arepalli, P.Nikolaev, R.E.Smalley, *Applied Physics.* **A72** (2001) 573.

[2] A.A. Puretzky, D.B. Geohegan, X. Fan, S.J. Pennycook - *Applied Physics.* **A70** (2000) 153.

[3] V.S. Burakov, N.V. Tarasenko, N.A. Savastenko, *Spectrochimica. Acta.* **B 56** 961 (2001).

[4] V.S.Burakov, A.F. Bokhonov, P.A.Naumenkov, M.I. Nedel'ko, and N.V.Tarasenko, *Zh. Prikl. Spectrosk.* **65** (1998) 426.

[5] V.S.Burakov, A.F. Bokhonov, P.A.Naumenkov, M.I. Nedel'ko, and N.V.Tarasenko, *Quantum Electronics* (in press).

[6] D.M.Gruen, S.Liu, A.R.Krauss, X.Pan *J Appl. Phys.* **75** (1994) 1758.